

3 RELEASE RATES FOR TOXIC SUBSTANCES

In Chapter 3

- 3.1 Estimation of worst-case release rates for toxic gases.
- 3.2 Estimation of release rates for toxic liquids evaporating from pools.
- 3.3 Estimation of release rates for common water solutions of toxic substances and for oleum.

This chapter describes simple methods for estimating release rates for regulated toxic substances for the worst-case scenario. Simple release rate equations are provided, and factors to be used in these equations are provided (in Appendix B) for each regulated substance. The estimated release rates may be used to estimate dispersion distances to the toxic endpoint for regulated toxic gases and liquids, as discussed in Chapter 4.

3.1 Release Rates for Toxic Gases

In Section 3.1

- 3.1.1 Method to estimate worst-case release rates for unmitigated releases (releases directly to the air) of toxic gas.
- 3.1.2 Method to estimate worst-case release rates for toxic gas in enclosures (passive mitigation).
- 3.1.3 Method to estimate worst-case release rates for liquefied refrigerated toxic gases in diked areas (as toxic liquid - see Section 3.2.3), including consideration of the duration of the release.

Regulated substances that are gases at ambient temperature (25 °C, 77 °F) should be considered gases for consequence analysis, with the exception of gases liquefied by refrigeration at atmospheric pressure. Gases liquefied under pressure should be treated as gases. Gases liquefied by refrigeration alone and released into diked areas may be treated as liquids at their boiling points if they would form a pool upon release that is more than one centimeter (0.033 foot) in depth. Gases liquefied by refrigeration alone that would form a pool one centimeter (0.033 foot) or less in depth should be treated as gases. Modeling shows that the evaporation rate from such a pool would be equal to or greater than the rate for a toxic gas, which is assumed to be released over 10 minutes; therefore, treating liquefied refrigerated gases as gases rather than liquids in such cases is reasonable. You may consider passive mitigation for gaseous releases and releases of gases liquefied by refrigeration.

3.1.1 Unmitigated Releases of Toxic Gas

If no passive mitigation system is in place, estimate the release rate for the release over a 10-minute period of the largest quantity resulting from a pipe or vessel failure, as required by the rule (40 CFR 68.25(c)). For a release from a vessel, calculate the release rate as follows:

$$QR = \frac{QS}{10} \quad (3-1)$$

where: QR = Release rate (pounds per minute)
 QS = Quantity released (pounds)

Example 1. Gas Release (Diborane)

You have a tank containing 2,500 pounds of diborane gas. Assuming the total quantity in the tank is released over a 10-minute period, the release rate (QR), from Equation 3-1, is:

$$QR = 2,500 \text{ pounds} / 10 \text{ minutes} = 250 \text{ pounds per minute}$$

3.1.2 Releases of Toxic Gas in Enclosed Space

If a gas is released in an enclosure such as a building or shed, the release rate to the outside air may be lessened considerably. The dynamics of this type of release are complex; however, you may use the simplified method presented here to estimate an approximate release rate to the outside air from a release in an enclosed space. The mitigation factor (i.e., 55 percent) presented in this method assumes that the release occurs in a fully enclosed, non-airtight space that is directly adjacent to the outside air. If you are modeling a release in an interior room that is enclosed within a building, a smaller factor (i.e., more mitigation) may be appropriate. On the other hand, a larger factor (i.e., less mitigation) should be used for a space that has doors or windows that could be open during a release. If any of these special circumstances apply to your site, you may want to consider performing site-specific modeling to determine the appropriate amount of passive mitigation. In addition, you should not incorporate the passive mitigation effect of building enclosures into your modeling if you have reason to believe the enclosure would not withstand the force of the release or if the chemical is handled outside the building (e.g., moved from one building to another building).

For the worst case, assume as before that the largest quantity resulting from a pipe or vessel failure is released over a 10-minute period. Determine the unmitigated worst-case scenario release rate of the gas as the quantity released divided by 10 (Equation 3-1). The release rate from the building will be approximately 55 percent of the worst-case scenario release rate (see Appendix D, Section D.1.2 for the derivation of this factor). Estimate the mitigated release rate as follows:

$$QR = \frac{QS}{10} \times 0.55 \quad (3-2)$$

where: QR = Release rate (pounds per minute)
 QS = Quantity released (pounds)
0.55 = Mitigation factor (discussed in Appendix D, Section D.1.2)

Example 2. Gas Release in Enclosure (Diborane)

Suppose the diborane gas from Example 1 is released inside a building at the rate of 250 pounds per minute. The mitigated release to the outside air from the building would be:

$$QR = 250 \text{ pounds/minute} \times 0.55 = 138 \text{ pounds per minute}$$

3.1.3 Releases of Liquefied Refrigerated Toxic Gas in Diked Area

If you have a toxic gas that is liquefied by refrigeration alone, and it will be released into an area where it will be contained by dikes to form a pool more than one centimeter (0.033 foot) in depth, you may carry out the worst-case analysis assuming evaporation from a liquid pool at the boiling point of the liquid. If your gas liquefied by refrigeration would form a pool one centimeter (0.033 foot) or less in depth, use the methods described in Section 3.1.1 or 3.1.2 above for the analysis. For a release in a diked area, first compare the diked area to the maximum area of the pool that could be formed. You can use Equation 3-6 in Section 3.2.3 to estimate the maximum size of the pool. Density factors (DF), needed for Equation 3-6, for toxic gases at their boiling points are listed in Exhibit B-1 of Appendix B. If the pool formed by the released liquid would be smaller than the diked area, assume a 10-minute gaseous release, and estimate the release rate as described in Section 3.1.1. If the dikes prevent the liquid from spreading out to form a pool of maximum size (one centimeter in depth), you may use the method described in Section 3.2.3 for mitigated liquid releases to estimate a release rate from a pool at the boiling point of the released substance. Use Equation 3-8 in Section 3.2.3 for the release rate. The Liquid Factor Boiling (LFB) for each toxic gas, needed to use Equation 3-8, is listed in Exhibit B-1 of Appendix B. See the example release rate estimation on the next page.

After you have estimated the release rate, estimate the duration of the vapor release from the pool (the time it will take for the pool to evaporate completely) by dividing the total quantity spilled by the release rate. You need to know the duration of release to choose the appropriate reference table of distances to estimate the consequence distance, as discussed in Section 4. (You do not need to consider the duration of the release for chlorine or sulfur dioxide, liquefied by refrigeration alone. Only one reference table of distances is provided for worst-case releases of each of these substances, and these tables may be used regardless of the release duration. The principal reason for making no distinction between 10-minute and longer releases for the chemical-specific tables is that the differences between the two are small relative to the uncertainties that have been identified.)

Example 3. Mitigated Release of Gases Liquefied by Refrigeration (Chlorine)

You have a refrigerated tank containing 50,000 pounds of liquid chlorine at ambient pressure. A diked area around the chlorine tank of 275 square feet is sufficient to hold all of the spilled liquid chlorine. Once the liquid spills into the dike, it is then assumed to evaporate at its boiling point (-29 °F). The evaporation rate at the boiling point is determined from Equation 3-8. For the calculation, wind speed is assumed to be 1.5 meters per second and the wind speed factor is 1.4, LFB for chlorine (from Exhibit B-1) is 0.19, and A is 275 square feet. The release rate is:

$$QR = 1.4 \times 0.19 \times 275 = 73 \text{ pounds per minute}$$

The duration of the release does not need to be considered for chlorine.

3.2 Release Rates for Toxic Liquids

In Section 3.2

- 3.2.1 Method to estimate the quantity of toxic liquid that could be released from a broken pipe.
- 3.2.2 Method to estimate the release rate of a toxic liquid evaporating from a pool with no mitigation (no dikes or enclosures), including:
 - Releases at ambient temperature (25 °C),
 - Releases at elevated temperature, and
 - Estimation of the duration of the release.
- 3.2.3 Method to estimate the release rate of a toxic liquid evaporating from a pool with passive mitigation, including:
 - Releases in diked areas,
 - Releases into other types of containment, and
 - Releases into buildings.
- 3.2.4 Estimation of release rates for mixtures containing toxic liquids.
- 3.2.5 Method to correct the estimated release rate for liquids released at temperatures between 25 °C and 50 °C.

For the worst-case analysis, the release rate to air for toxic liquids is assumed to be the rate of evaporation from the pool formed by the released liquid. This section provides methods to estimate the evaporation rate. Assume the total quantity in a vessel or the maximum quantity from pipes is released into the pool. Passive mitigation measures (e.g., dikes) may be considered in determining the area of the pool and

the release rate. To estimate the consequence distance using this guidance, you must estimate how long it will take for the pool to evaporate (the duration of the release), as well as the release rate, as discussed below.

The rule (40 CFR 68.22(g)) requires you to assume that liquids (other than gases liquefied by refrigeration) are released at the highest maximum daily temperature for the previous three years or at process temperature, whichever is higher. This chapter provides methods to estimate the release rate at 25 °C (77 °F) or at the boiling point, and also provides a method to correct the release rate at 25 °C for releases at temperatures between 25 °C and 50 °C.

The calculation methods provided in this section apply to substances that are liquids under ambient conditions or gases liquefied by refrigeration alone that are released to form pools deeper than one centimeter (see Section 3.1.3 above). You must treat gases liquefied under other conditions (under pressure or a combination of pressure and refrigeration) or gases liquefied by refrigeration alone that would form pools one centimeter or less in depth upon release as gas rather than liquid releases (see Sections 3.1.1 and 3.1.2 above).

3.2.1 Releases of Toxic Liquids from Pipes

To consider a liquid release from a broken pipe, estimate the maximum quantity that could be released assuming that the pipe is full of liquid. To estimate the quantity in the pipe, you need to know the length of the pipe (in feet) and cross-sectional area of the pipe (in square feet). Note also that liquid may be released from both directions at a pipe shear (both in the direction of operational flow and the reverse direction, depending on the location of the shear). Therefore, the length would be the full length of pipe carrying the liquid on the facility grounds. Then, the volume of the liquid in the pipe (in cubic feet) is the length of the pipe times the cross-sectional area. The quantity in the pipe (in pounds) is the volume divided by the Density Factor (DF) times 0.033. (DF values are listed in Appendix B, Exhibit B-2. Density in pounds per cubic foot is equal to 1/(DF times 0.033).) Assume the estimated quantity (in pounds) is released into a pool and use the method and equations described below in Section 3.2.2 (unmitigated releases) or 3.2.3 (releases with passive mitigation) to determine the evaporation rate of the liquid from the pool.

3.2.2 Unmitigated Releases of Toxic Liquids

If no passive mitigation measures are in place, the liquid is assumed to form a pool one centimeter (0.39 inch or 0.033 foot) deep instantaneously. You may calculate the release rate to air from the pool (the evaporation rate) as discussed below for releases at ambient or elevated temperature.

Ambient Temperature

If the liquid is always at ambient temperature, find the Liquid Factor Ambient (LFA) and the Density Factor (DF) in Exhibit B-2 of Appendix B. The LFA and DF apply to liquids at 25 °C; if your ambient temperature is between 25 °C and 50 °C, you may use the method described here and then apply a Temperature Correction Factor (TCF), as discussed in Section 3.2.5 below, to correct the calculated release rate. Calculate the release rate of the liquid at 25 °C from the following equation:

$$QR = QS \times 1.4 \times LFA \times DF \quad (3-3)$$

where:

QR	=	Release rate (pounds per minute)
QS	=	Quantity released (pounds)
1.4	=	Wind speed factor = $1.5^{0.78}$, where 1.5 meters per second (3.4 miles per hour) is the wind speed for the worst case
LFA	=	Liquid Factor Ambient
DF	=	Density Factor

Example 4. Unmitigated Liquid Release at Ambient Temperature (Acrylonitrile)

You have a tank containing 20,000 pounds of acrylonitrile at ambient temperature. The total quantity in the tank is spilled onto the ground in an undiked area, forming a pool. Assume the pool spreads out to a depth of one centimeter. The release rate from the pool (QR) is calculated from Equation 3-3. For the calculation, the wind speed is assumed to be 1.5 meters per second and the wind speed factor is 1.4. From Exhibit B-2, Appendix B, LFA for acrylonitrile is 0.018 and DF is 0.61. Then:

$$QR = 20,000 \times 1.4 \times 0.018 \times 0.61 = 307 \text{ pounds per minute}$$

The duration of the release (from Equation 3-5) would be:

$$t = 20,000 \text{ pounds} / 307 \text{ pounds per minute} = 65 \text{ minutes}$$

Elevated Temperature

If the liquid is at an elevated temperature (above 50 °C or at or close to the boiling point), find the Liquid Factor Boiling (LFB) and the Density Factor (DF) in Exhibit B-2 of Appendix B (see Appendix D, Section D.2.2, for the derivation of these factors). For temperatures up to 50 °C, you may use the method above for ambient temperature and apply the Temperature Correction Factors, as discussed in Section 3.2.5. If the temperature is above 50 °C, or the liquid is at or close to its boiling point, or no Temperature Correction Factors are available for your liquid, calculate the release rate of the liquid from the following equation:

$$QR = QS \times 1.4 \times LFB \times DF \quad (3-4)$$

where:

QR	=	Release rate (pounds per minute)
QS	=	Quantity released (pounds)
1.4	=	Wind speed factor = $1.5^{0.78}$, where 1.5 meters per second (3.4 miles per hour) is the wind speed for the worst case
LFB	=	Liquid Factor Boiling
DF	=	Density Factor

Example 5. Unmitigated Release at Elevated Temperature (Acrylonitrile)

You have a tank containing 20,000 pounds of acrylonitrile at an elevated temperature. The total quantity in the tank is spilled onto the ground in an undiked area, forming a pool. Assume the pool spreads out to a depth of one centimeter. The release rate from the pool is calculated from Equation 3-4. For the calculation, the wind speed factor for 1.5 meters per second is 1.4. From Exhibit B-2, Appendix B, LFB for acrylonitrile is 0.11 and DF is 0.61. Then:

$$QR = 20,000 \times 1.4 \times 0.11 \times 0.61 = 1,880 \text{ pounds per minute}$$

The duration of the release (from Equation 3-5) would be:

$$t = 20,000 \text{ pounds} / 1,880 \text{ pounds per minute} = 11 \text{ minutes}$$

Duration of Release

After you have estimated a release rate as described above, determine the duration of the vapor release from the pool (the time it will take for the liquid pool to evaporate completely). If you calculate a corrected release rate for liquids above 25 °C, use the corrected release rate, estimated as discussed in Section 3.2.5 below, to estimate the release duration. To estimate the time in minutes, divide the total quantity released (in pounds) by the release rate (in pounds per minute) as follows:

$$t = \frac{QS}{QR} \quad (3-5)$$

where:

t	=	Duration of the release (minutes)
QR	=	Release rate (pounds per minute) (use release rate corrected for temperature, QR_C , if appropriate)
QS	=	Quantity released (pounds)

You will use the duration of the vapor release from the pool to decide which table is appropriate for estimating distance, as discussed in Chapter 4 below.

3.2.3 Releases of Toxic Liquids with Passive Mitigation

Diked Areas

If the toxic liquid will be released into an area where it will be contained by dikes, compare the diked area to the maximum area of the pool that could be formed; the smaller of the two areas should be used in determination of the evaporation rate. The maximum area of the pool (assuming a depth of one centimeter) is:

$$A = QS \times DF \quad (3-6)$$

where:

A	=	Maximum area of pool (square feet) for depth of one centimeter
QS	=	Quantity released (pounds)
DF	=	Density Factor (listed in Exhibit B-2, Appendix B)

Maximum Area Smaller than Diked Area. If the maximum area of the pool is smaller than the diked area, calculate the release rate as described for "no mitigation" above.

Diked Area Smaller than Maximum Area. If the diked area is smaller than the maximum pool area, go to Exhibit B-2 in Appendix B to find the Liquid Factor Ambient (LFA), if the liquid is at ambient temperature, or the Liquid Factor Boiling (LFB), if the liquid is at an elevated temperature. For liquids at temperatures between 25 °C and 50 °C, you may use the method described here and then apply a Temperature Correction Factor (TCF), as discussed in Section 3.2.5 below, to correct the calculated release rate. For gases liquefied by refrigeration alone, use LFB from Exhibit B-1. Calculate the release rate from the diked area as follows for liquids at ambient temperature:

$$QR = 1.4 \times LFA \times A \quad (3-7)$$

or, for liquids at elevated temperature or for gases liquefied by refrigeration alone:

$$QR = 1.4 \times LFB \times A \quad (3-8)$$

where:

QR	=	Release rate (pounds per minute)
1.4	=	Wind speed factor = $1.5^{0.78}$, where 1.5 meters per second (3.4 miles per hour) is the wind speed for the worst case
LFA	=	Liquid Factor Ambient (listed in Exhibit B-2, Appendix B)
LFB	=	Liquid Factor Boiling (listed in Exhibit B-1 (for liquefied gases) or B-2 (for liquids), Appendix B)
A	=	Diked area (square feet)

Potential Overflow of Diked Area. In case of a large liquid spill, you also need to consider whether the liquid could overflow the diked area. Follow these steps:

- Determine the volume of the diked area in cubic feet from surface area times depth or length times width times depth (in feet).
- Determine the volume of liquid spilled in cubic feet from $QS \times DF \times 0.033$ ($DF \times 0.033$ is equal to 1/density in pounds per cubic foot).
- Compare the volume of the diked area to the volume of liquid spilled. If the volume of liquid is greater than the volume of the diked area:
 - Subtract the volume of the diked area from the total volume spilled to determine the volume that might overflow the diked area.

- Estimate the maximum size of the pool formed by the overflowing liquid (in square feet) by dividing the overflow volume (in cubic feet) by 0.033 (the depth of the pool in feet).
- Add the surface area of the diked area and the area of the pool formed by the overflow to estimate the total pool area (A).
- Estimate the evaporation rate from Equation 3-7 or 3-8 above.

After you have estimated the release rate, estimate the duration of the vapor release from the pool by dividing the total quantity spilled by the release rate (Equation 3-5 above).

Example 6. Mitigated Liquid Release at Ambient Temperature (Bromine)

You have a tank containing 20,000 pounds of bromine at an ambient temperature of 25 °C. Assume that the total quantity in the tank is spilled into a square diked area 10 feet by 10 feet (area 100 square feet). The dike walls are four feet high. The area (A) that would be covered to a depth of 0.033 feet (one centimeter) by the spilled liquid is given by Equation 3-6 as the quantity released (QS) times the Density Factor (DF). From Exhibit B-2, Appendix B, DF for bromine is 0.16. Then:

$$A = 20,000 \times 0.16, \text{ or } 3,200 \text{ square feet}$$

The diked area is smaller than the maximum pool area. The volume of bromine spilled is $20,000 \times 0.16 \times 0.033$, or 106 cubic feet. The spilled liquid would fill the diked area to a depth of a little more than one foot, well below the top of the wall. You use the diked area to determine the evaporation rate from Equation 3-7. For the calculation, wind speed is 1.5 meters per second, the wind speed factor is 1.4, LFA for bromine (from Exhibit B-2) is 0.073, and A is 100 square feet. The release rate is:

$$QR = 1.4 \times 0.073 \times 100 = 10 \text{ pounds per minute}$$

The maximum duration of the release would be:

$$t = 20,000 \text{ pounds} / 10 \text{ pounds per minute} = 2,000 \text{ minutes}$$

Other Containment

If the toxic liquid will be contained by other means (e.g., enclosed catch basins or trenches), consider the total quantity that could be spilled and estimate the surface area of the released liquid that potentially would be exposed to the air. Look at the dimensions of trenches or other areas where spilled liquids would be exposed to the air to determine the surface area of pools that could be formed. Use the instructions above to estimate a release rate from the total surface area.

Releases into Buildings

If the toxic liquid is released inside a building, compare the area of the pool that would be formed (depending upon floor space or passive mitigation) to the maximum area of the pool that could be formed (if the liquid is not contained); the smaller of the two areas should be used in determining the evaporation rate. The maximum area of the pool is determined as described above for releases into diked areas, using Equation 3-6. If the toxic liquid would spread to cover the building floor, you determine the area of the building floor as:

$$A = L \times W \quad (3-9)$$

where:

A	=	Area (square feet)
L	=	Length (feet)
W	=	Width (feet)

If there are obstacles such as dikes inside the building, determine the size of the pool that would be formed based on the area defined by the dikes or other obstacles.

The evaporation rate is then determined for a worst-case scenario (i.e., wind speed is 1.5 meters per second (3.4 miles per hour)), using Equation 3-3 or 3-4, if the liquid spreads to its maximum area, or Equation 3-7 or 3-8, if the pool area is smaller than the maximum. The maximum rate of evaporated liquid exiting the building is taken to be 10 percent of the calculated worst-case scenario evaporation rate (see Appendix D, Section D.2.4 for the derivation of this factor), as follows:

$$QR_B = 0.1 \times QR \quad (3-10)$$

where:

QR_B	=	Release rate from building
QR	=	Release rate from pool, estimated as discussed above
0.1	=	Mitigation factor, discussed in Appendix D, Section D.2.4

Note that the mitigation factor (i.e., 0.1) presented in this method assumes that the release occurs in a fully enclosed, non-airtight space that is directly adjacent to the outside air. It may not apply to a release in an interior room that is enclosed within a building, or to a space that has doors or windows that could be open during a release. In such cases, you may want to consider performing site-specific modeling to determine the appropriate amount of passive mitigation.

Example 7. Liquid Release Inside Building (Bromine)

Suppose that your tank of bromine from Example 6 is contained inside a storage shed 10 feet by 10 feet (area 100 square feet). There are no dikes inside the shed. From Example 6, you see that the area covered by the bromine in an unenclosed space would be 3,200 square feet. The building area is smaller than the maximum pool area; therefore, the building floor area should be used to determine the evaporation rate from Equation 3-7. For the calculation, first determine the worst-case scenario evaporation rate:

$$QR = 1.4 \times 0.073 \times 100 = 10 \text{ pounds per minute}$$

The release rate to the outside air of the evaporated liquid leaving the building would then be:

$$QR_B = 0.1 \times 10 \text{ pounds per minute} = 1 \text{ pound per minute}$$

3.2.4 Mixtures Containing Toxic Liquids

Mixtures containing regulated toxic substances do not have to be considered if the concentration of the regulated substance in the mixture is below one percent by weight or if you can demonstrate that the partial vapor pressure of the regulated substances in the mixture is below 10 millimeters of mercury (mm Hg). Regulated substances present as by-products or impurities would need to be considered if they are present in concentrations of one percent or greater in quantities above their thresholds, and their partial vapor pressures are 10 mm Hg or higher. In case of a spill of a liquid mixture containing a regulated toxic substance with partial vapor pressure of 10 mm Hg or higher (with the exception of common water solutions, discussed in the next section), you have several options for estimating a release rate:

- Carry out the analysis as described above in Sections 3.2.2 or 3.2.3 using the quantity of the regulated substance in the mixture and the liquid factor (LFA or LFB) and density factor for the regulated substance in pure form. This is a simple approach that likely will give conservative results.
- If you know the partial pressure of the regulated substance in the mixture, you may estimate a more realistic evaporation rate. An equation for the evaporation rate is given at the end of Section B.2 in Appendix B.
 - In this case, estimate a pool size for the entire quantity of the mixture, for an unmitigated release. If you know the density of the mixture, you may use it in estimating the pool size; otherwise, you may assume the density is the same as the pure regulated substance (in most cases, this assumption is unlikely to have a large effect on the results).
- You may estimate the partial pressure of the regulated substance in the mixture by the method described in Section B.2 in Appendix B and use the equation presented there to estimate an evaporation rate. This equation is appropriate to mixtures and solutions in

which the components do not interact with each other. It is probably inappropriate for most water solutions. It is likely to overestimate the partial vapor pressure of regulated substances in water solutions in which hydrogen bonding may occur (e.g., solutions of acids or alcohols). As discussed above, use the pool size for the entire quantity of the mixture for an unmitigated release.

Example 8. Mixture Containing Toxic Liquid (Acrylonitrile)

You have a tank containing 50,000 pounds of a mixture of acrylonitrile (a regulated substance) and N,N-dimethylformamide (not regulated). The weight of each of the components of the mixture is known (acrylonitrile = 20,000 pounds; N,N-dimethylformamide = 30,000 pounds.) The molecular weight of acrylonitrile, from Exhibit B-2, is 53.06, and the molecular weight of N,N-dimethylformamide is 73.09. Using Equation B-3, Appendix B, calculate the mole fraction of acrylonitrile in the solution as follows:

$$X_r = \frac{(20,000/53.06)}{(20,000/53.06) + (30,000/73.09)}$$

$$X_r = \frac{377}{377 + 410}$$

$$X_r = 0.48$$

Estimate the partial vapor pressure of acrylonitrile using Equation B-4 as follows (using the vapor pressure of acrylonitrile in pure form at 25 °C, 108 mm Hg, from Exhibit B-2, Appendix B):

$$VP_m = 0.48 \times 108 = 51.8 \text{ mm Hg}$$

Before calculating evaporation rate for acrylonitrile in the mixture, you must determine the surface area of the pool formed by the entire quantity of the mixture, using Equation 3-6. The quantity released is 50,000 pounds and the Density Factor for acrylonitrile is 0.61 in Exhibit B-2; therefore:

$$A = 50,000 \times 0.61 = 30,500 \text{ square feet}$$

Now calculate the evaporation rate for acrylonitrile in the mixture from Equation B-5 using the VP_m and A calculated above:

$$QR = \frac{0.0035 \times 1.0 \times (53.06)^{0.75} \times 30,500 \times 51.8}{298}$$

$$QR = 262 \text{ pounds per minute}$$

3.2.5 Release Rate Correction for Toxic Liquids Released at Temperatures Between 25 °C and 50 °C

If your liquid is at a temperature between 25 °C (77 °F) and 50 °C (122 °F), you must use the higher temperature for the offsite consequence analysis. You may correct the release rate calculated for a pool at 25

°C to estimate from a pool at the higher temperature using Temperature Correction Factors (TCF) provided in Appendix B, Exhibit B-4. Calculate a corrected release rate as follows:

- Calculate the release rate (QR) of the liquid at 25 °C (77 °F) as described in Section 3.2.2 (for unmitigated releases) or 3.2.3 (for releases with passive mitigation).
- From Exhibit B-4 in Appendix B:
 - Find your liquid in the left-hand column of the table.
 - Find the temperature closest to your temperature at the top of the table. If your temperature is at the midpoint between two temperatures, go to the higher temperature; otherwise go to the closest temperature (higher or lower than your temperature).
 - Find the TCF for your liquid in the column for the appropriate temperature.
- Estimate a corrected release rate (QR_c) by multiplying the estimated release rate by the TCF; i.e.,

$$QR_c = QR \times TCF \quad (3-11)$$

where: QR_c = Corrected release rate
 QR = Release rate calculated for 25 °C
 TCF = Temperature Correction Factor (from Exhibit B-4, Appendix B)

The derivation of the Temperature Correction Factors is discussed in Appendix D, Section D.2.2. If you have vapor pressure-temperature data for a liquid not covered in Exhibit B-4, you may correct the evaporation rate using the method presented in Section D.2.2.

Example 9. Liquid Release at Ambient Temperature Between 25 °C and 50 °C (Bromine)

Assume the tank containing 20,000 pounds of bromine, from Example 6, is at an ambient temperature of 35 °C (95 °F). As in Example 6, the total quantity in the tank is spilled into a diked enclosure that completely contains the spill. The surface area is 100 square feet. In Example 6, the release rate (QR) at 25 °C was calculated from Equation 3-7 to be 10 pounds per minute. To adjust the release rate for the temperature of 35 °C, you find the Temperature Correction Factor (TCF) for bromine at 35 °C from Exhibit B-4 in Appendix B. The TCF at this temperature is 1.5; the corrected release rate (QR_c) at 35 °C, from Equation 3-11, is

$$QR_c = 10 \times 1.5 = 15 \text{ pounds per minute}$$

The duration of the release (from Equation 3-5) would be:

$$t = 20,000 \text{ pounds} / 15 \text{ pounds per minute} = 1,300 \text{ minutes}$$

3.3 Release Rates for Common Water Solutions of Toxic Substances and for Oleum

In Section 3.3

- Methods to estimate the release rates for several common water solutions and for oleum, including:
 - Evaporation from pools with no mitigation (see 3.2.2),
 - Evaporation from pools with dikes (see 3.2.3),
 - Releases at elevated temperatures of solutions of gases, and
 - Releases at elevated temperatures of solutions of liquids.

This section presents a simple method of estimating the release rate from spills of water solutions of several substances. Oleum (a solution of sulfur trioxide in sulfuric acid) also is discussed in this section.

The vapor pressure and evaporation rate of a substance in solution depends on its concentration in the solution. If a concentrated water solution containing a volatile toxic substance is spilled, the toxic substance initially will evaporate more quickly than water from the spilled solution, and the vapor pressure and evaporation rate will decrease as the concentration of the toxic substance in the solution decreases. At much lower concentrations, water may evaporate more quickly than the toxic substance. There is one concentration at which the composition of the solution does not change as evaporation occurs. For most situations of interest, the concentration exceeds this concentration, and the toxic substance evaporates more quickly than water.

For estimating release rates from solutions, this guidance lists liquid factors (ambient) for several common water solutions at several concentrations that take into account the decrease in evaporation rate with decreasing concentration. Exhibit B-3 in Appendix B provides LFA and DF values for several concentrations

of ammonia, formaldehyde, hydrochloric acid, hydrofluoric acid, and nitric acid in water solution. Factors for oleum are also included in the exhibit. Chlorine dioxide also may be found in water solutions; however, solutions of chlorine dioxide commonly are below one percent concentration. Solutions below one percent concentration do not have to be considered. Chlorine dioxide, therefore, is not included in Exhibit B-3. These factors may be used to estimate an average release rate for the listed substances from a pool formed by a spill of solution. Liquid factors are provided for two different wind speeds, because the wind speed affects the rate of evaporation.

For the worst case, use the factor for a wind speed of 1.5 meters per second (3.4 miles per hour). You need to consider only the first 10 minutes of the release for solutions under ambient conditions in estimating the consequence distance, because the toxic component in a solution evaporates fastest during the first few minutes of a spill, when its concentration is highest. Modeling indicates that analysis considering the first 10 minutes of the release gives a good approximation of the overall consequences of the release. Although the toxic substance will continue to evaporate from the pool after 10 minutes, the rate of evaporation is so much lower that it can safely be ignored in estimating the consequence distance. (See Appendix D, Section D.2.3, for more information.) Estimate release rates as follows:

Ambient Temperature

- Unmitigated. If no passive mitigation measures are in place, and the solution is at ambient temperature, find the LFA at 1.5 meters per second (3.4 miles per hour) and DF for the solution in Appendix B, Exhibit B-3. Follow the instructions for liquids presented in Section 3.2.2 above to estimate the release rate of the listed substance in solution. Use the total quantity of the solution as the quantity released (QS) in carrying out the calculation of release rate.
- Mitigated. If passive mitigation is in place, and the solution is at ambient temperature, find the LFA at 1.5 meters per second (3.4 miles per hour) in Appendix B, Exhibit B-3, and follow the instructions for liquids in Section 3.2.3 above. Use the total quantity of the solution to estimate the maximum pool area for comparison with the diked area.

Example 10. Evaporation Rate for Water Solution at Ambient Temperature (Hydrochloric Acid)

You have a tank containing 50,000 pounds of 37 percent hydrochloric acid solution, at ambient temperature. For the worst-case analysis, you assume the entire contents of the tank is released, forming a pool. The release occurs in a diked area of 9,000 square feet.

From Exhibit B-3, Appendix B, the Density Factor (DF) for 37 percent hydrochloric acid is 0.42. From Equation 3-6, the maximum area of the pool would be 50,000 times 0.42, or 21,000 square feet. The diked area is smaller; therefore, the diked area should be used in the evaporation rate (release rate) calculation, using Equation 3-7.

For the calculation using Equation 3-7, you need the pool area (9,000 square feet) and the Liquid Factor Ambient (LFA) for 37 percent hydrochloric acid; you assume a wind speed of 1.5 meters per second, so the wind speed factor is 1.4. From Exhibit B-3, Appendix B, the LFA is 0.0085. From Equation 3-7, the release rate (QR) of hydrogen chloride from the pool is:

$$QR = 1.4 \times 9,000 \times 0.0085 = 107 \text{ pounds per minute}$$

You do not need to consider the duration of the release, because only the first ten minutes are considered.

Elevated Temperature

- Known Vapor Pressure. If the solution is at an elevated temperature, the vapor pressure of the regulated substance and its release rate from the solution will be much higher. This guidance does not include temperature correction factors for evaporation rates of regulated substances from solutions. If you know the partial vapor pressure of the toxic substance in solution at the relevant temperature, you can carry out the calculation of the release rate using the equations in Appendix D, Sections D.2.1 and D.2.2. As for releases of solutions at ambient temperature, you only need to consider the first 10 minutes of the release, because the evaporation rate of the toxic substance from the solution will decrease rapidly as its concentration decreases.
- Unknown Vapor Pressure. If you do not know the vapor pressure of the substance in solution, as a conservative approach for the worst-case analysis, use the appropriate instructions, as follows:
 - *Solutions containing substances that are gases under ambient conditions.* The list of regulated substances includes several substances that, in their pure form, are gases under ambient conditions, but that may commonly be found in water solutions. These substances include ammonia, formaldehyde, hydrogen chloride, and hydrogen fluoride. For a release of a solution of ammonia, formaldehyde, hydrochloric acid, or hydrofluoric acid above ambient temperature, if you do not have vapor pressure data for the temperature of interest or prefer a simpler method, assume the quantity of the pure substance in the solution is released as a gas over 10

minutes, as discussed in Section 3.1 above. You may determine the amount of pure substance in the solution from the concentration (e.g., a solution of 37 percent hydrochloric acid by weight would contain a quantity of hydrogen chloride equal to 0.37 times the total weight of the solution).

Example 11. Evaporation Rate for Gas in Water Solution at Elevated Temperature (Hydrochloric Acid)

You have 50,000 pounds of 37 percent hydrochloric acid solution in a high-temperature process. For the worst-case analysis, you assume the entire contents of the process vessel is released. In this case, because the solution is at an elevated temperature, you consider the release of gaseous hydrogen chloride from the hot solution.

The solution would contain $50,000 \times 0.37$ pounds of hydrogen chloride, or 18,500 pounds. You assume the entire 18,500 pounds is released over 10 minutes. From Equation 3-1, the release rate is 18,500 divided by 10, or 1,850 pounds per minute.

- Liquids in solution. If you have vapor pressure data for the liquid in solution (including nitric acid in water solution and sulfur trioxide in oleum) at the temperature of interest, you may use that data to estimate the release rate, as discussed above. You only need to consider the first 10 minutes of the evaporation.

For a release of nitric acid solution at a temperature above ambient, if you do not have vapor pressure data or prefer to use this simpler method, determine the quantity of pure nitric acid in the solution from the concentration. Assume the quantity of pure nitric acid is released at an elevated temperature and estimate a release rate as discussed in Section 3.2 above, using the LFB. For temperatures between 25 °C and 50 °C, you may use the LFA and the temperature correction factors for the pure substance, as described in Section 3.2.5. You do not need to estimate the duration of the release, because you only consider the first 10 minutes.

Similarly, for a release of oleum at an elevated temperature, determine the quantity of free sulfur trioxide in the oleum from the concentration and assume the sulfur trioxide is released at an elevated temperature. Use the LFB or the LFA and temperature correction factors for sulfur trioxide to estimate a release rate as discussed in Section 3.2. You only need to consider the first 10 minutes of the release in your analysis.

For a spill of liquid in solution into a diked area, you would need to consider the total quantity of solution in determining whether the liquid could overflow the diked area (see the steps in Section 3.2.3). If you find that the liquid could overflow the dikes, you would need to consider both the quantity of pure substance remaining inside the diked area and the quantity of pure substance spilled outside the diked area in carrying out the release rate analysis as discussed in Section 3.2.3.

Example 12. Evaporation Rate for Liquid in Water Solution at Elevated Temperature (Nitric Acid)

You have 18,000 pounds of 90 percent nitric acid solution in a high temperature process. The solution would contain $18,000 \times 0.90$ pounds of nitric acid, or 16,200 pounds. You assume 16,200 pounds of pure nitric acid is released at an elevated temperature.

For the calculation using Equation 3-4, you need the quantity released (16,200); the Liquid Factor Boiling (LFB) for nitric acid (0.12 from Exhibit B-2); the Density Factor (DF) for nitric acid (0.32 from Exhibit B-2); and you assume a wind speed of 1.5 meter per second, so the wind speed factor is 1.4. From Equation 3-4, the release rate (QR) of hot nitric acid is:

$$QR = 16,200 \times 1.4 \times 0.12 \times 0.32 = 870 \text{ pounds per minute}$$

You do not need to estimate the duration of release, because you only consider the first 10 minutes.